Exploiting the dynamic properties of Pt on ceria for low temperature CO oxidation†

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Supporting information

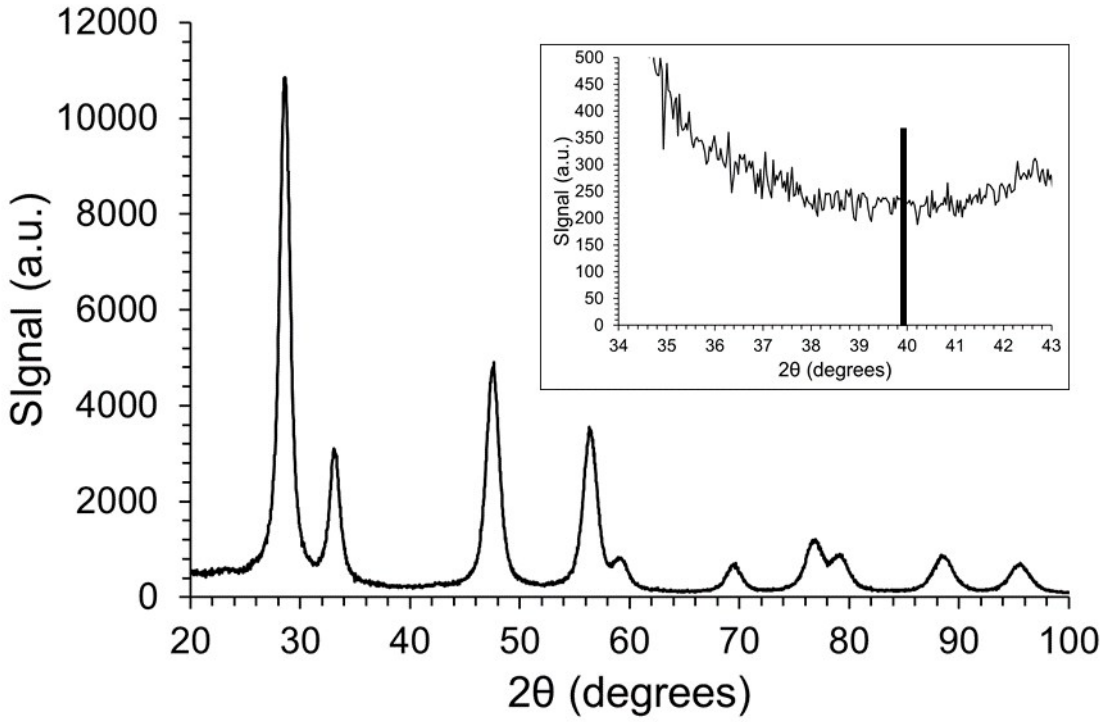

Figure S1: Diffraction pattern of the Pt/CeO_2 catalyst after an oxidation step for 1 h in 20% O_2 at 500 °C. All peaks correspond to the Fm-3m cubic structure of ceria (JCPDS 00-34-0394). Inset: zoom of the XRD pattern between 34 and 43°, the bar indicates the theoretical position of the more intense diffraction peak of Pt^0 (2θ = 39.9°, JCPDS 00-004-802).

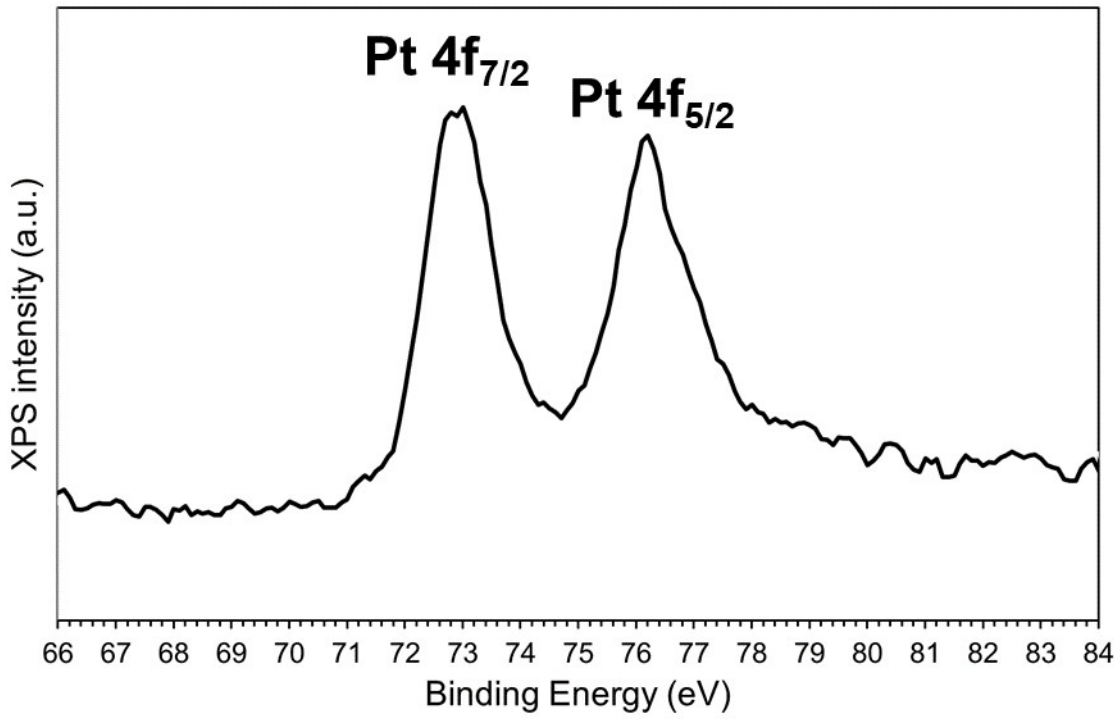

Figure S2: Pt 4f XPS spectrum of the Pt/CeO_2 catalyst at the reference state.

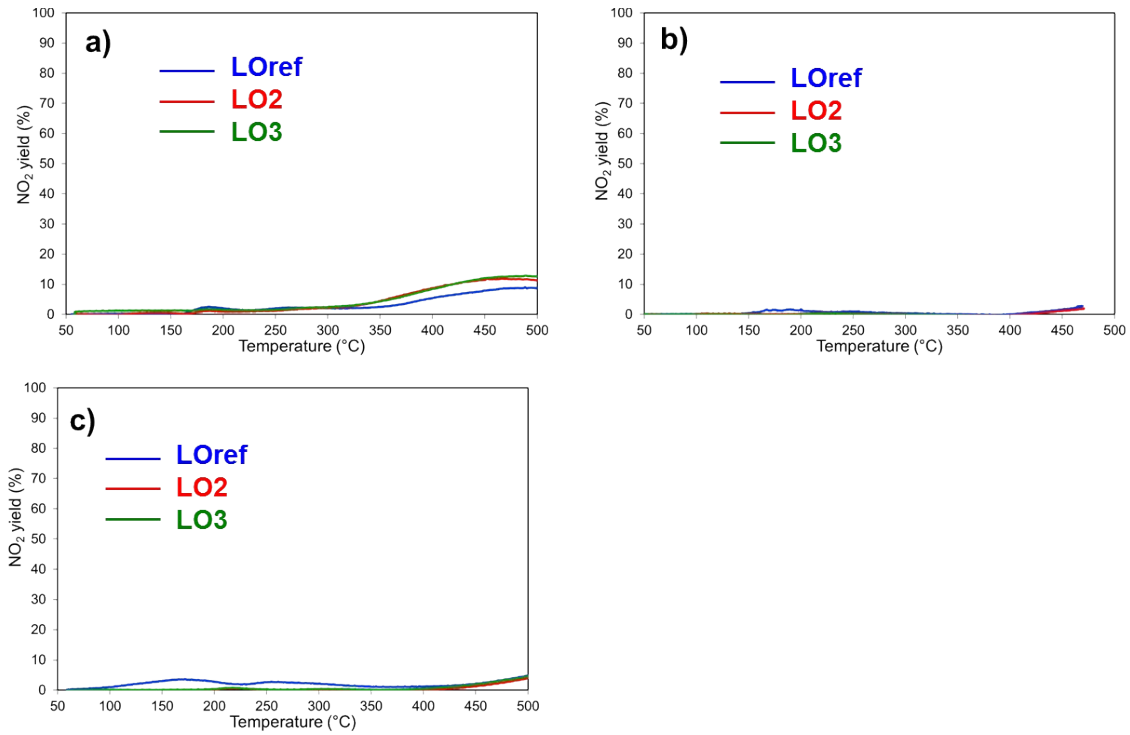

Figure S3. Impact of the REDOX sequence on the NO_2 yield of Pt/CeO_2: a) Red_{500}/Ox_{500}, b) Red_{250}/Ox_{250} and c) Red_{250}/Ox_{RT}. Lean mixture: $[C_3H_6]$ = 500 ppm, [CO] = 1000 ppm, [NO] = 500 ppm, $[O_2]$ = 10% and $[H_2O]$ = 10%. Note that LOref curves in a), b) and c) are not identical due to slightly different Pt loadings in the SiC/catalyst mixtures.

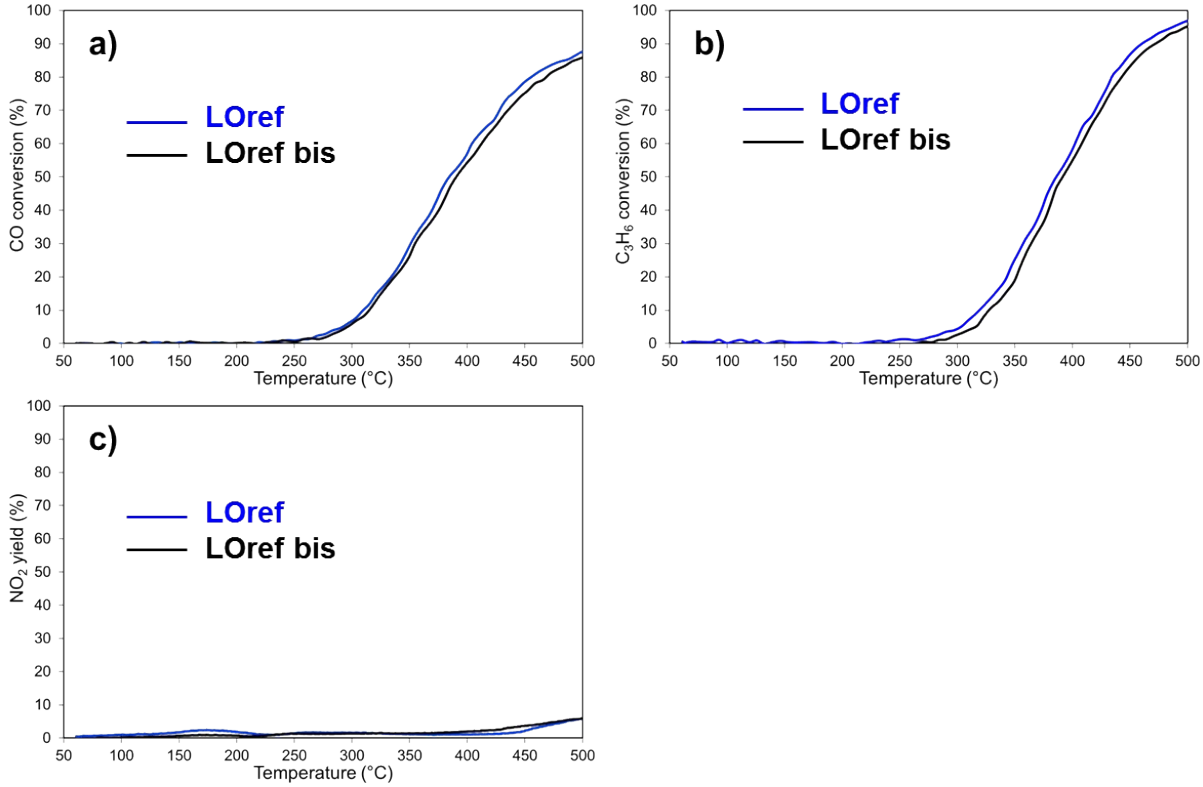

Figure S4. Two successive LOref light-off curves : a) CO conversion b) C_3H_6 conversion and c) NO_2 yield. Lean mixture: [C_3H_6] = 500 ppm, [CO] = 1000 ppm, [NO] = 500 ppm, [O_2] = 10% and [H_2O] = 10%.

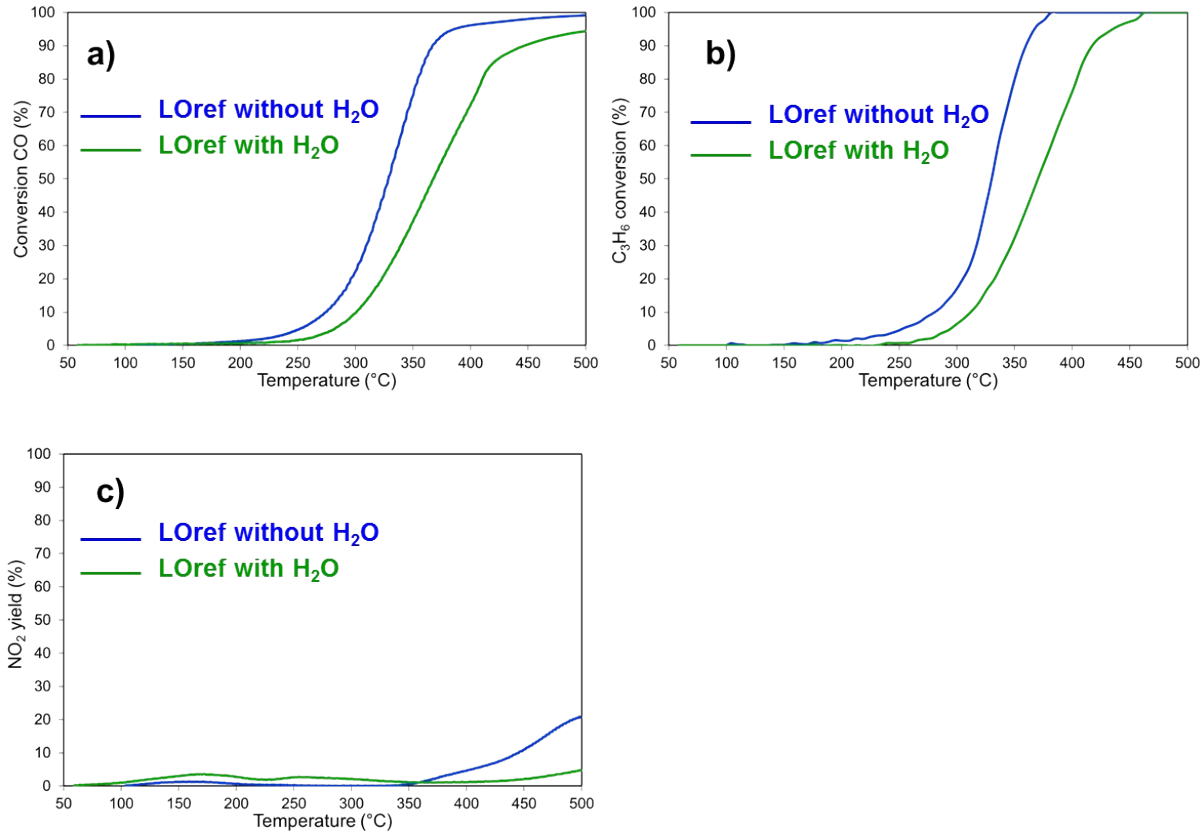

Figure S5. Impact of the presence of water on the LOref performances: a) CO conversion b) C_3H_6 conversion and c) NO_2 yield. Lean mixture: [C_3H_6] = 500 ppm, [CO] = 1000 ppm, [NO] = 500 ppm, [O_2] = 10% and [H_2O] = 0 or 10%.

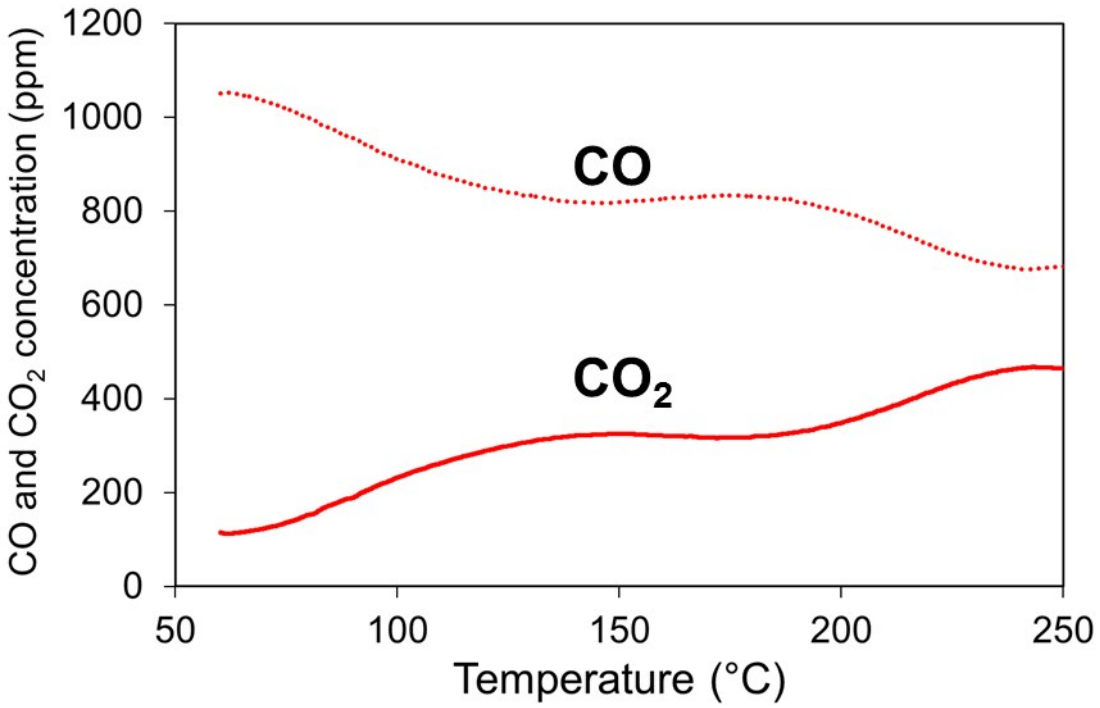

Figure S6. CO and CO_2 concentration profiles versus temperature during LO2 after a Red_{250}/Ox_{RT} sequence.

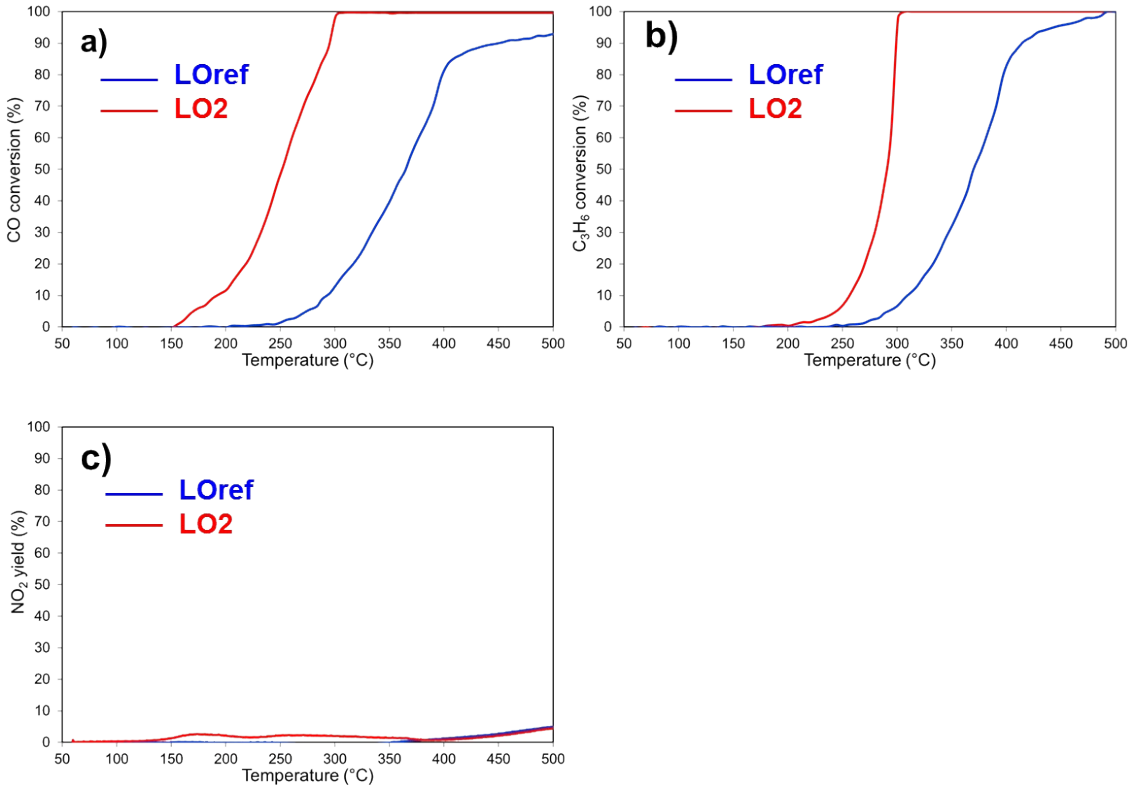

Figure S7. Impact of a lean/rich pulse cycling at 250 °C on the catalytic performances of Pt/CeO_2: a) CO conversion b) C_3H_6 conversion and c) NO_2 yield. The pulses sequence were composed of 30 s in 2% CO/He followed by 90 s in the lean mixture cycled for 1 h. Lean mixture : $[C_3H_6]$ = 500 ppm, [CO] = 1000 ppm, [NO] = 500 ppm, $[O_2]$ = 10% and $[H_2O]$ = 10%.

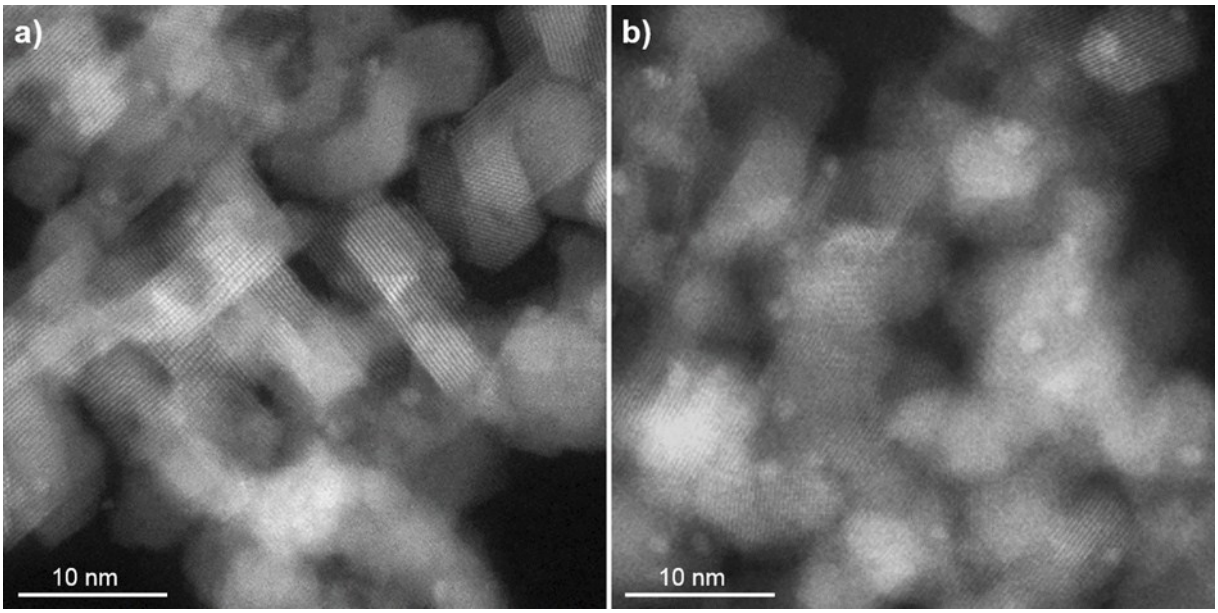

Figure S8. Representative STEM images of Pt/CeO_2 a) after a reduction at 500 °C for 1 h in 10% H_2/He and b) after a reduction at 250 °C for 1 h in 10% H_2-He.

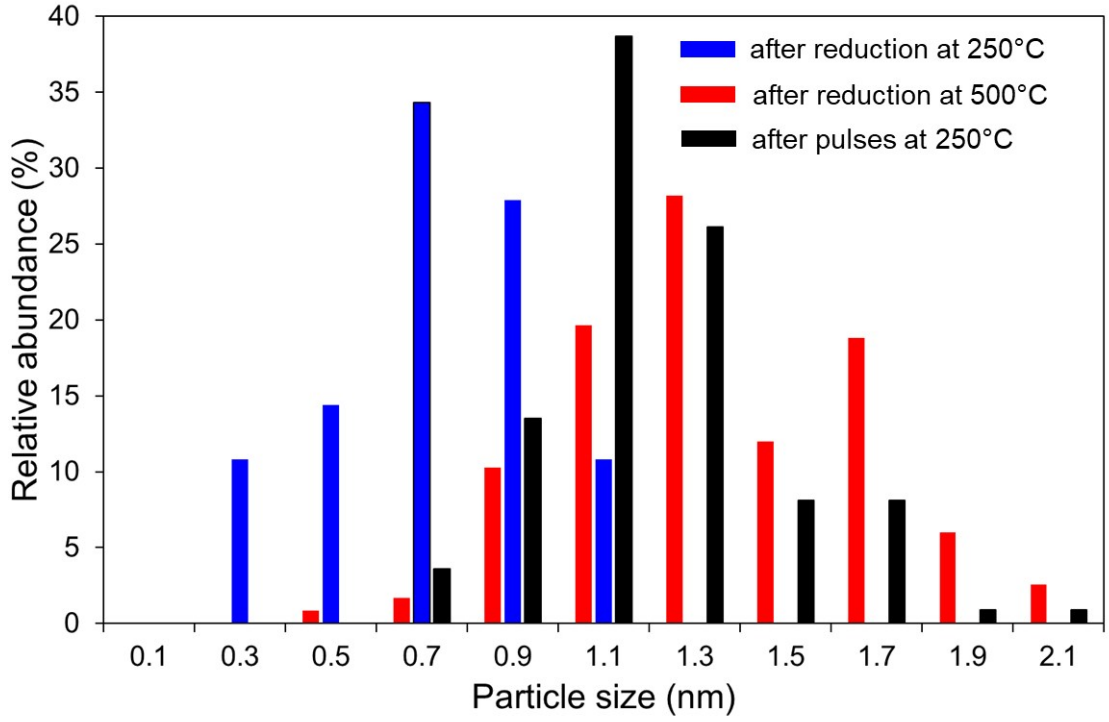

Figure S9. Particle size histogram of the Pt/CeO_2 catalyst after a reduction either at 250 °C or 500 °C for 1 h in 10% H_2/He and after a pulse cycling at 250°C for 1 h (90 s in the lean mixture and 30 s in 2% CO/He). The size distribution was based on around 100 particles. Projected mean equivalent diameter: 0.83 nm (σ= 0.23 nm) after a reduction at 250 °C, 1.46 nm (σ = 0.33 nm) after a reduction at 500 °C and 1.30 nm (σ = 0.26 nm) after pulse cycling at 250°C.

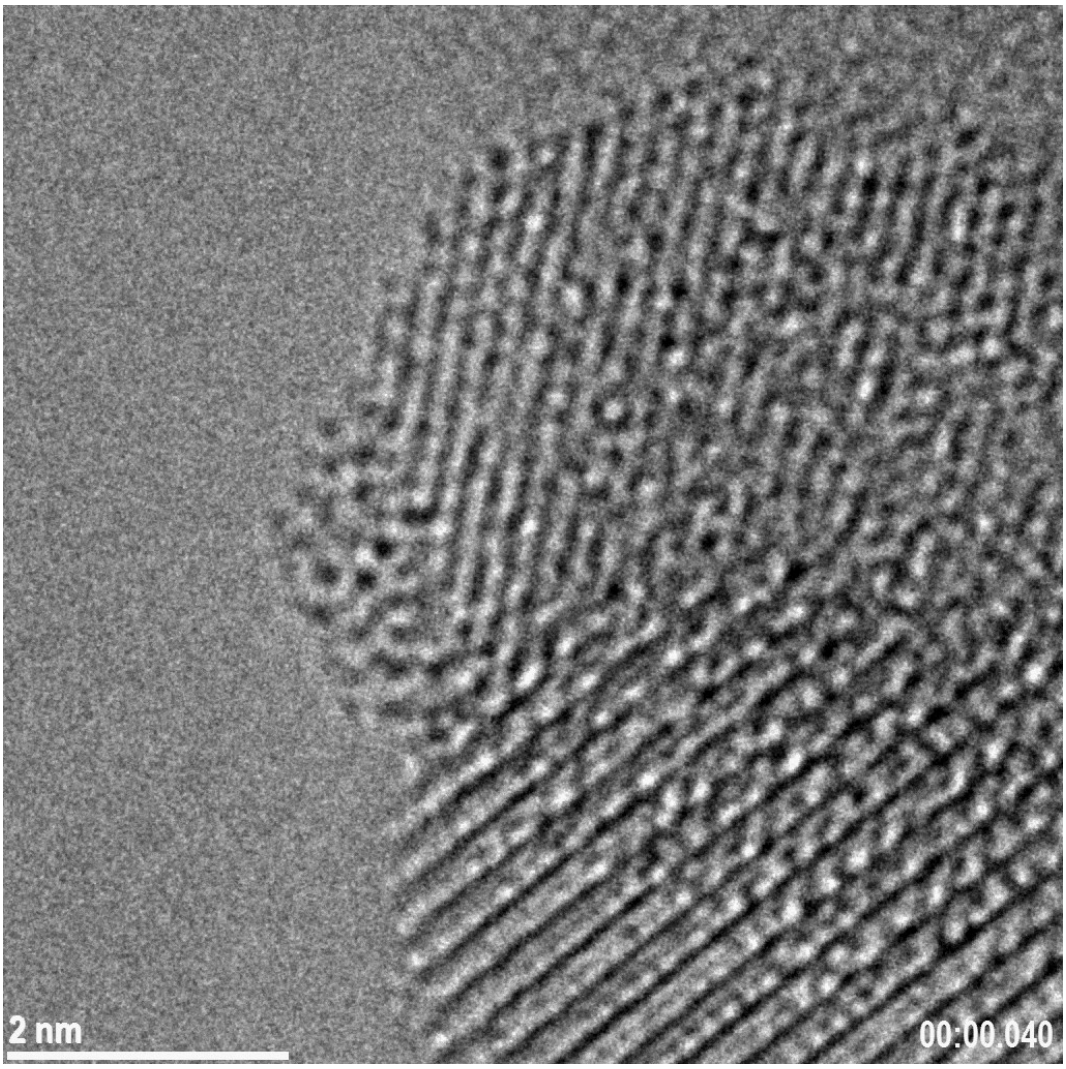

Figure S10. Video of a Pt cluster produced after a Red_{250}/Ox_{250} at RT in high vacuum (High Resolution TEM mode).

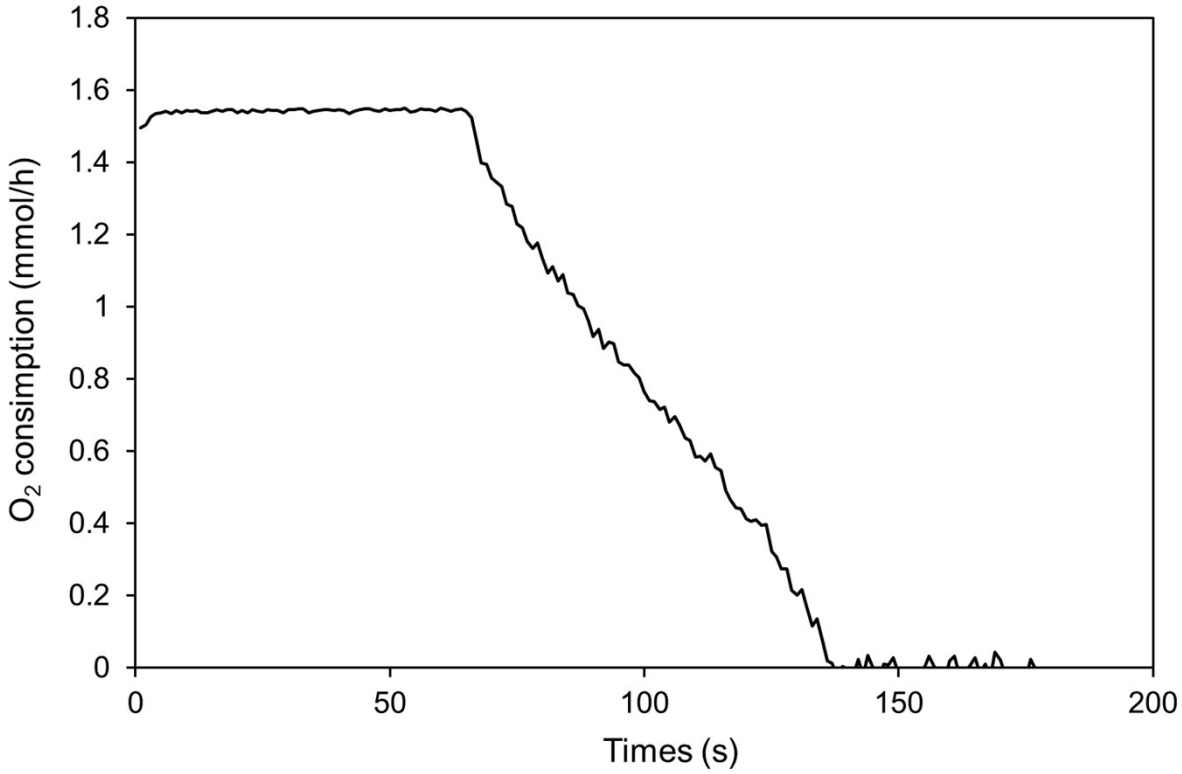

Figure S11: Variation of the O_2 consumption of the Pt/CeO_2 catalyst as a function of time at room temperature after a TPR (1% H_2/He) up to 250°C (10°C/min) and a plateau at 250°C for 1 h in 10% H_2/He.

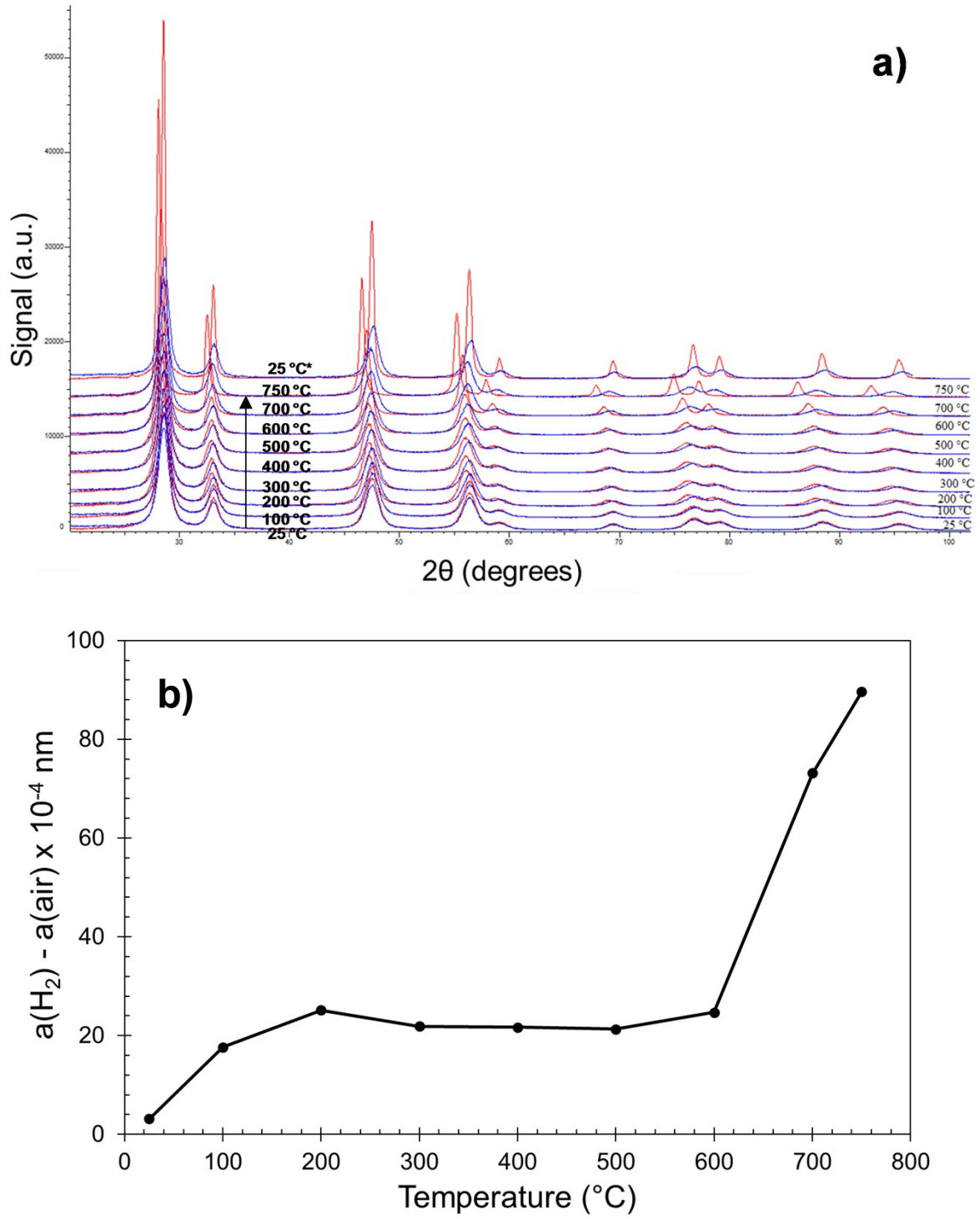

Figure S12. a) Raw diffraction patterns of a fresh Pt/CeO_2 catalyst (in its reference state) recorded in air (blue) and in H_2 (red) as a function of the temperature between 25 and 750 °C. 25* : XRD recorded at 25°C in air or H_2 after the cooling from 750°C in the same atmosphere. b) Variation of the ceria lattice parameter extracted from a) between H_2 and air thermal treatment as a function of the temperature.

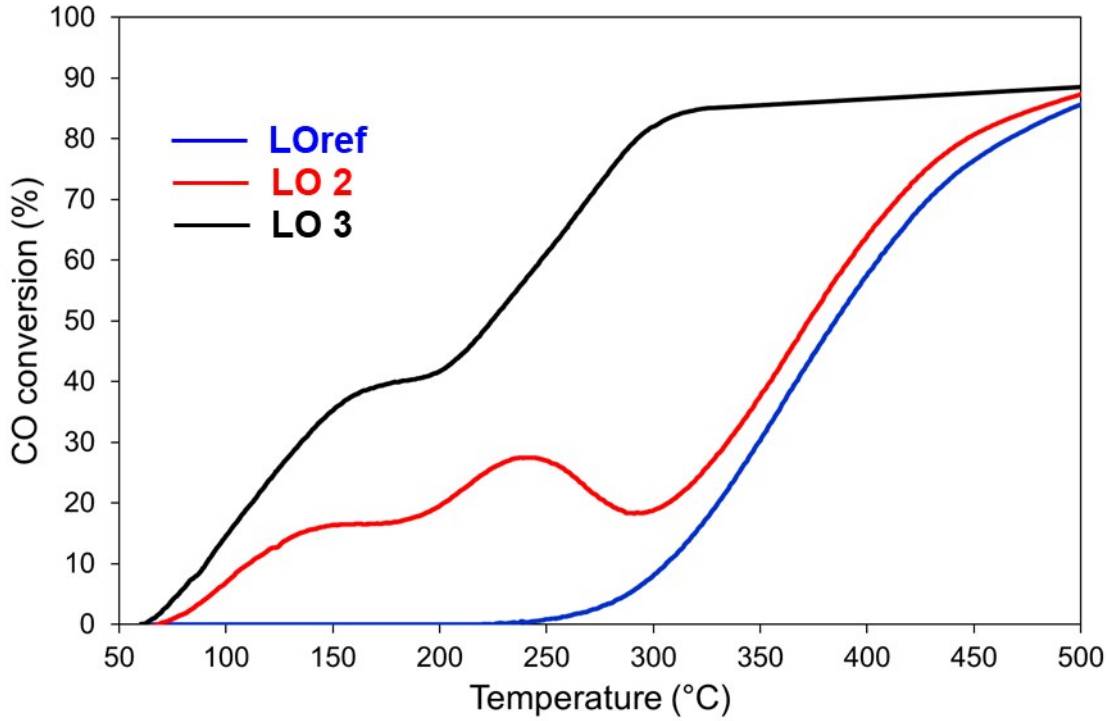

Figure S13: Variations of the CO conversion as a function of the temperature: LOref after an oxidation step for 1 h in 20% O_2 at 500 °C mixture, LO 2: after a Red_{250}/Ox_{RT} sequence and LO 3: after a Red_{250}/Ox_{RT} sequence but without any propene in the feed. Reactive mixture: [C_3H_6] = 0 / 500 ppm, [CO] = 1000 ppm, [NO] = 500 ppm, [O_2] = 10% and [H_2O] = 10%.

Table S1 : Comparison of the CO oxidation rates and TOF (Turn-Over Frequency) values at 100°C for various Pt/CeO_2 catalysts from literature and in this work.

Species and conditioning	Specific surface area (m^2/g)	Pt loading (wt.%) and precursor	Reaction conditions	WHSV ($L \cdot g^{-1} \cdot catalyst \cdot h^{-1}$)	rCO (mmol/s/g Pt)	TOF ($x10^{-2}$ s^{-1})	Ref
Subnanometric thin Pt clusters after $Red_{250}Ox_{RT}$	125	0.88 $Pt(NH_3)_4(NO_3)_2$	[CO]=1000 ppm, [C_3H_6] = 500 ppm, [NO] = 500 ppm, [O_2]= 10%, [H_2O] = 10%	750	0.198	4-6 Estimated for Pt dispersion between 60 and 100%	This work
Pt nanoparticles After redox pulses at 250°C	30	1 $Pt(NH_3)_4(NO_3)_2$	[CO]=1000 ppm, [C_3H_6] = 500 ppm, [O_2]= 8%	600	0.17	6 Estimated for a Pt dispersion of 50%	[1]
Pt-O-Pt clusters After a reduction at 200°C in 5% H_2 and a subsequent exposure to CO/O_2 feed between 100 and 185°C	80	0.27 H_2PtCl_6	[CO]=1000 ppm, [O_2]= 5%, [H_2O] = 5%. No propene.	2400	10	196	[2]
Single atom After a steam treatment at 750°C	25.6	1 H_2PtCl_6	[CO]=4000 ppm, [C_3H_6] = 100 ppm, [NO] = 500 ppm, [O_2]= 10%, [H_2O] = 5%	200	0.181	3.5	[3]
Nanoparticles after a calcination at 800°C 10 h and a reduction at 275°C for 1 h in CO (8% in He)	38	1 $Pt(NH_3)_4(NO_3)_2$	[CO]=1.9%, [O_2]= 1.3%	232	1.05	20.6 (calculated from the total number of Pt atoms)	[4]

References

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[2] H. Wang, J.-X. Liu, L.F. Allard, S. Lee, J. Liu, H. Li, J. Wang, J. Wang, S.H. Oh, W. Li, M. Flytzani-Stephanopoulos, M. Shen, B.R. Goldsmith, M. Yang, Surpassing the single-atom catalytic activity limit through paired Pt-O-Pt ensemble built from isolated Pt1 atoms, Nat. Commun. 10 (2019). doi:10.1038/s41467-019-11856-9.

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[4] X.I. Pereira-Hernández, A. DeLaRiva, V. Muravev, D. Kunwar, H. Xiong, B. Sudduth, M. Engelhard, L. Kovarik, E.J.M. Hensen, Y. Wang, A.K. Datye, Tuning Pt-CeO_2 interactions by high-temperature vapor-phase synthesis for improved reducibility of lattice oxygen, Nat. Commun. 10 (2019). doi:10.1038/s41467-019-09308-5.